JP 61-146591 (4 July 1986) (54) INK JET RECORDING MEDIUM

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1. NAME OF THE INVENTION

Ink jet recording medium

2. CLAIM

Ink jet recording medium, with regard to ink jet recording mediums that form recording image using aqueous ink that contains water soluble dye, having as distinctive feature that that recording medium contains a hindered amine type compound.

3. DETAILED EXPLANATION OF THE INVENTION

(A) Industrial field of application

Our invention concerns recording mediums that do the recording by using ink, and more particularly it concerns recording mediums for ink jet, with which the images and letters that are recorded on top of the medium have a high density, and with which the absorption property and preservation property of the recording image are excellent.

(B) Prior state of the art and problem points

Ink jet recording methods carry out recording of images, letters, etc. by letting very small droplets of ink fly by means of various operation principles, and let them attach to a recording medium like paper, etc., and they have as distinctive features that it is easy to make them high speed, low noice and multi-color, that the flexibility property of the recording pattern is big, and further that development and fixing are not necessary, etc., so that they are rapidly becoming popular for various applications as recording installations of all kinds of figures and color images, etc., including Chinese characters. Further, for the image that is formed by means of a multi-color ink jet method, it is possible to obtain a recording that has no inferiority compared to image by means of color photography methods or multi-color prints by means of plate-making methods, and since it is cheaper than photography technology as far as applications for which only a few-copies need to be prepared are concerned, they are being widely applied up to the field of full color image recording.

As for recording mediums that are used in these ink jet recording methods, efforts have been made from the point of the ink compositions and installations that must use high quality paper or coated paper, which is used for normal printing and recording. However, following the improvement of the capacities of the ink jet recording installations, such as the increased speed of the installation, higher precision, becoming full color, etc., and the

wider range of applications, more advanced characteristics are being required for the recording medium as well. In other words, it is required of these recording mediums that the density of the ink dots is high, that the color tone is clear and vivid, that the absorption of the ink is quick, so that the ink does not run out or blur even in case ink dots are accumulated, that the spread in horizontal direction of the ink dots is not bigger than necessary, and the circumference is smooth and does not become hazy, and further that the resistance of the dye does not decrease, and preferably increases, in case the recording image is exposed to ultraviolet rays, oxygen in the air or water, etc.

In order to solve these problems, a number of proposals have been made in the past. For example, in Tokkai 52-53012, a paper for ink jet recording is described, for which paint for surface processing is moistened on low size raw paper, and in Tokkai 53-49113 a paper for ink jet recording is described, for which water soluble high molecules are impregnated in a sheet in which urea - formalin resin powder was added. These papers for ink jet recording of the normal paper type have a fast ink absorption, but they have the flaws that the circumference of the dots easily becomes blurry, and the dot density is low. In Tokkai 55-5830 we also have a description of a paper for ink jet recording, for which an ink absorbing coat layer is placed on the surface of a support, and in Tokkai 55-51583 there is the description of an example that uses non-colloidal silica powder as pigment in the cover layer, while in Tokkai 55-11829 an example of daubed paper that uses a twolayer structure with different ink absorption speeds is described. These papers for ink jet recording of the coated paper type are better than papers for ink jet recording of the normal paper type in the points of the dot diameter and dot form, the dot density and the reproduction property of the color tone, but inks that make use of these recording mediums are often aqueous inks that water soluble dye, and in case water, etc. is poured on the image that is formed on top of the recording medium, there is the problem point that the dye dissolves again, and blurs, which considerably decreases the value of the recorded matters.

So, in order to improve these flaws, we have descriptions, for example in Tokkai 55-53591, of an example that supplies water soluble salt of metal on the recording surface, in Tokkai 56-84992 an example of a recording medium that contains a polycation high molecular electrolyte on the surface, or in Tokkai 55-150396 a method which supplies an agent to make water resistant, which forms lake and dye inside the ink after ink jet recording, and further in Tokkai 56-58869 a method to make water resistant by making a water soluble high molecule insoluble after doing ink jet recording on a recording sheet on which that water soluble high molecule was coated.

However, the effect of these methods to make water resistant has been weak, or else the agent to make water resistant provokes some kind of reaction with the dye, which makes the preservation property of the dye deteriorate, so that it has been quite difficult to let sufficient water resistance and light resistance be compatible.

So, in order to improve the light resistance, there is, for example, the description of examples in Tokkai 54-68303, 54-85804 and 56-18151, in which ultraviolet ray absorption agent is added in the ink solution. However, these ultraviolet ray absorption agents have the problem that they let the jet stability of the ink deteriorate, and that they have little effect when only a small amount is added. As another means of solution it has been proposed in Tokkai 57-74192, 57-74193 and 57-87988 to include ultraviolet ray absorption agent like benzo phenone type, benzo triazole type, etc in the ink jet recording

sheet on the other hand, but since it does not dissolve in water in large quantity, it was difficult to obtain sufficient ultraviolet ray absorption effect, and in case it was used after being emulsified, etc. it was impossible to sufficiently display an effect through the influence of the emulsifying agent.

(C) Aim of the invention

The aim of our invention is to present a recording medium with an improved ink jet adaptability such as mentioned earlier, with which the aqueous ink image is excellent in water resistance and light resistance, and which particularly has improved discoloring resistance and light resistance of water soluble black dye and / or water soluble magenta dye.

(D) Structure and Working of the invention

In other words, our invention is an ink jet recording medium, with regard to ink jet recording mediums that form recording image using aqueous ink that contains water soluble dye, having as distinctive feature that that recording medium contains a hindered amine type compound.

What we mean by hindered amine type compound in our invention is a compound that has one or more hindered amines in the molecule, as represented by Formula (I) below.

Formula (I) See Japanese text p. 3

(In the formula, R_5 is a hydrogen atom or an alkyl group of $C_1 \sim C_8$, a benzyl group, an allyl group, an acetyl group, etc., and preferably it is a hydrogen atom or a methyl group. R_1 , R_2 , R_3 , R_4 are lower alkyl groups, carbonyl groups, etc., and preferably they are methyl groups and / or ethyl groups. When n=1, A is $-NH_2$, -OH, $=CH_2$, =O, -R, -OR, -OCO-R, $-NHCH_2$ CH_2 CH_2 OCH_3 , -NHCSSH, etc. (here R is an alkyl group, See Japanese text p. 3, etc.).

In case n = 2, it is See Japanese text p. 3 (m is $1 \sim 14$), See Japanese text p. 3, - NH (CH₂)₃ NH - , See Japanese text p. 3 (M is a bivalent metal atom), etc. Or A can also be a polymer.

As the hindered amine type compounds that are represented by this general formula, we have hindered amines that have a piperidine structure, for example 4 - benzoyl oxy - 2, 2, 6, 6 - tetra methyl piperidine, bis - (2, 2, 6, 6 - tetra methyl - 4 - N - methyl)piperidyl) sebacate, di -(1, 2, 2, 6, 6 - penta methyl - 4 - piperidyl) - 2 - n - butyl - 2 -(3, 5 - di - t butyl - 4 - hydroxy benzyl) malonate, bis -(2, 2, 6, 6 - tetra methyl - 4 carbonyl oxy piperidino) – P – dimethyl benzyl, 2, 2, 4, 4 – tetra methyl – 7 - oxa - 3, 20 - diaza – 21 – oxo – dispiro $[5 \cdot 1 \cdot 9 \cdot 19]$ heneikosan (?), bis – (2, 2, 6, 6 - tetra methyl – 4 – piperidinyl) sebacate, dimethyl succinate, 2 – (4 - hydroxy - 2, 2, 6, 6 – tetra methyl – 1 – piperidinyl) ethanol condensation product and poly [$\{6 - (1, 1, 3, 3 - \text{tetra methyl})\}$ butyl) imino $\} - 1$, 3, 5 – triazine – 2, 4 – diyl – $\{4 - (2, 2, 6, 6 - \text{tetra methyl piperidinyl})\}$ imino\ - hexamethylene - $\{4 - (2, 2, 6, 6 - \text{tetra methyl piperidinyl}) \text{ imino}\}\]$ and the like. Among these we can preferably use bis -(2, 2, 6, 6 - tetra methyl - 4 - piperidyl)malonate, bis -(2, 2, 6, 6 - tetra methyl - 4 - piperidyl) sebacate, bis -(2, 2, 6, 6 - tetra)methyl - 4 - piperidyl) phtalate, 2, 2, 6, 6 - tetra methyl - 4 - piperidyl benzoate, 4 amino -2, 2, 6, 6 - tetra methyl piperidine, 2, 2, 6, 6 - tetra methyl -4 - piperidinole, etc. It is also no problem whatsoever to jointly use benzo triazole type or benzo phenone type ultraviolet ray absorption agents or hindered phenol type anti-oxidation agents with these hindered amine type compounds. Further, in order to make them applicable for recording mediums, it is also possible to make them into organic acid or inorganic acid



salts, introduce a water soluble group, emulsify them, or dissolve them as they are in water or a suitable solvent, and use them that way. The contained amount inside the recording medium is $0.001^{\circ} \sim 20 \text{ mimol} / \text{m}^2$, preferably $0.005 \sim 10 \text{ mmol} / \text{m}^2$, as number of the hindered amine group.

As production method of the recording medium that has the hindered amine type compound mentioned earlier in our invention, we have the methods that incorporate it by dipping or coating a coating solution, in which the hindered amine type compound was dissolved or dispersed, with a suitable coating machine like a size press installation, which is placed along the way, when disaggregating the pulp fibers to get slurry and making paper with a paper making machine, the methods that coat a coating solution, which contains the hindered amine type compound, on a suitable support using a normal coating device, and place an ink reception layer, which contains the hindered amine type compound, and further the methods that coat the hindered amine type compound, which was dissolved or dispersed on top of an ink reception layer consisting of adhesive agent and ink absorbing pigment, etc. In these cases we can jointly use the cover material, pigments, adhesive agents and other additives that are normally used. Also, if it is necessary to give the image water resistance, it is possible to jointly use cationic resin, and in our invention it is rather advisable to actively use it, in order to improve the water resistance and the light resistance at the same time.

As cover material or pigment that can be used in our invention, we have light calcium carbonate, heavy calcium carbonate, kaolin, talc, calcium sulfate, barium sulfate, titanium oxide, zinc oxide, zinc sulfide, zinc carbonate, satin white, aluminum silicate, diatomaceous earth, calcium silicate, magnesium silicate, synthetic amorphous silica, aluminum hydroxide, alumina, lithopone and such white pigments, and as organic pigments, styrene type plastic pigment, acryl type plastic pigment, microcapsules, urea resin pigment, etc. In our invention, we preferably can use synthetic amorphous silica and aluminum hydroxide among these.

What we call cationic resin in our invention indicates a monomer, oligomer or polymer that dissociates and gives cationic property when it dissolves in water, and preferably it is a compound that has a quarternary ammonium group, and especially preferably it has a structure represented in the general formula's $(I) \sim (VI)$ below.

(I) See Japanese text p. 4

In the formula, R_1 , R_2 , R_3 represent an alkyl group, m is $1 \sim 7$, n is $2 \sim 10$, and Y represents an acid group.

(II) See Japanese text p. 4 (III) See Japanese text p. 4

(IV) See Japanese text p. 4

In formula's (II) \sim (IV), R_1 , R_2 represent - CH_3 , - CH_2 - CH_3 , - CH_2 - CH_2 - OH, and Y represents an acid group.

(V) polyalkylene polyamine dicyan diamido ammonium salt condensation product As the compounds that are represented with general formula (I), we can name for example Narpoly – 607 (made by Narco Chemical Co.) or Polyfix 601 (made by Showa Kobunshi Co.).

The compounds that are represented with general formulas (II) \sim (IV) are polydiallyl amine derivatives, and are obtained by means of cyclic polymerisation of diallyl amine compounds, and we can name for example Bacore (Bakall?) 1697 (made by Aride

Colloid Co.), Cat Floc (Calgon Corp), PAS (Nitto Boseki Co.), Neofix RPD (made by Nikka Kagaku Co.), etc.

Further, as the compounds that are represented with general formula (V), we can name for example Neofix RP - 70 (made by Nikka Kagaku Co.).

The contained amount of these cationic resins that are represented with general formulas (I) \sim (V) is normally 0.1 \sim 4 g/m², and preferably 0.2 \sim 2 g/m².

As adhesive agents that can be used in our invention, we can use, separately or in a composition, for example starch oxide, etherified starch, carboxy methyl cellulose, hydroxy ethyl cellulose, and such cellulose derivatives, casein, gelatin, soybean albumin, polyvinyl alcohol and its derivatives, maleic anhydride resin, normal styrene - butadiene copolymer, methyl methacrylate - butadiene copolymer and such conjugate diene type polymer latex, acryl type polymer latex like polymer or copolymer of ester acrylate and ester methacrylate, vinyl type polymer latex like ethylene vinyl acetate copolymer, or else functional group modified polymer latex of every kind of these polymers by means of monomer containing a functional group like a carboxyl group, melamine resin, urea resin, and such thermal hardening synthetic resin type aqueous adhesive agents, polymethyl methacrylate, polyurethane resin, unsaturated polyester resin, vinyl chloride - vinyl acetate copolymer, polyvinyl butyral, alkyd resin and such synthetic resin type adhesive agent. These adhesive agents are normally used at $2 \sim 120$ parts, preferably $5 \sim 50$ parts against 100 parts of pigment, but there is no particular limitation to their ratio as long as it is a sufficient amount for the adhesion of the pigment. However, when we use more than 120 parts of adhesive agent, it's not favorable because it decreases the aperture structure due to the film building of the adhesive agent, or the apertures become extermely small.

As other additives we can suitably include pigment dispersion agents, thickening agents, fluidity modification agents, defoaming agents, foam control agents, mold release agents, foaming agents, penetrating agents, coloring dye, coloring pigment, fluorescent whitening agents, ultraviolet ray absorption agents, anti-oxidation agents, anti-mold agents, anti-bacteria agents, agents to make waterproof, etc.

As support, we can use sheet shaped substances like paper or thermoplastic resin film. In the case of paper, it does not matter whether or not cover material is included, with paper for which moderate sizing was implemented or else no sizing agent was added.

And in the case of thermoplastic film, we can use polyester, polystyrene, polyvinyl chloride, polymethyl methacrylate, cellulose acetate, polyethylene, polycarbonate and such transparent film, or white-colored non-transparent film by means of minute foaming or filling of white pigment. As white pigment that can be filled, we can use plenty of substances like, for example, titanium oxide, calcium sulfate, calcium carbonate, silica, clay, talc, zinc oxide, etc.

It is also possible to use so-called laminate paper, etc., which is processed by means of fused resin, sticking together these resin films on a surface of paper. It is also okay to implement corona electric discharge treatment or have an undercoat layer in order to improve the adhesion of the ink reception layer and these resin surfaces.

Sheets that are merely coated on top of a support can be used just like that as sheets for recording in our invention, but it is also possible to give the surface smoothness by passing it through a heating and / or pressure roll nip with, for example, a supercalender or crosscalender. In this case, unreasonable processing by means of supercalender processing lets the ink absorption by way of the apertures between the grains, that have

carefully been formed, deteriorate, and therefore it sometimes happens that the degree of processing is limited.

What we call aqueous ink in our invention is a recording medium that consists of the adhesive agent mentioned below, a liquid medium and other additives.

As adhesive agent we can preferably use direct dyes, acid dyes, basic dyes, reactive dyes or pigments for food, and such water soluble dyes.

We are for a second	and direct dyon.
We can name for example	e, as unecoluyes:
C. I. Direct Black	2, 4, 9, 11, 14, 17, 19, 22, 27, 32, 36, 38, 41, 48, 49, 51, 56, 62, 71, 74, 75, 77, 78, 80, 105, 106, 107, 108, 112, 113, 117, 132,
	146, 154, 194
C. I. Direct Yellow	1, 2, 4, 8, 11, 24, 26, 27, 28, 33, 34, 39, 41, 42, 44, 48, 50, 51,
	58, 72, 85, 86, 87, 88, 98, 100, 110
C. I. Direct Orange	6, 8, 10, 26, 29, 39, 41, 49, 51, 102
C. I. Direct Red	1, 2, 4, 8, 9, 11, 13, 17, 20, 23, 24, 28, 31, 33, 37, 39, 44, 46,
	47, 48, 51, 59, 62, 63, 73, 75, 77, 80, 81, 83, 84, 85, 90, 94, 99,
	101, 108, 110, 145, 189, 197, 220, 224, 225, 226, 227, 230
C. I. Direct Violet	1, 7, 9, 12, 35, 48, 51, 90, 94
C. I. Direct Blue	1, 2, 6, 8, 15, 22, 25, 34, 69, 70, 71, 72, 75, 76, 78, 80, 81, 82,
	83, 86, 90, 98, 106, 108, 110, 120, 123, 158, 163, 165, 192,
	193, 194, 195, 196, 199, 200, 201, 202, 203, 207, 218, 236,
	237, 239, 246, 258
C. I. Direct Green	1, 6, 8, 28, 33, 37, 63, 64
C. I. Direct Braun	1 A, 2, 6, 25, 27, 44, 58, 95, 100, 101, 106, 112, 173, 194
As acid dyes:	4 2 7 46 47 24 26 22 21 41 42 52 52 62 62 24 127
C. I. Acid Black	1, 2, 7, 16, 17, 24, 26, 28, 31, 41, 48, 52, 58, 60, 63, 94, 107,
	109, 112, 118, 119, 121, 122, 131, 155, 156
C. I. Acid Yellow	1, 3, 4, 7, 11, 12, 13, 14, 17, 18, 19, 23, 25, 29, 34, 36, 38, 40,
	41, 42, 44, 49, 53, 55, 59, 61, 71, 72, 76, 78, 99, 111, 114, 116,
G T A 110	122, 135, 161, 172
C. I. Acid Orange	7, 8, 10, 33, 56, 64
C. I. Acid Red	1, 4, 6, 8, 13, 14, 15, 18, 19, 21, 26, 27, 30, 32, 34, 35, 37, 40,
	42, 51, 52, 54, 57, 80, 82, 83, 85, 87, 88, 89, 92, 94, 97, 106,
	108, 110, 115, 119, 129, 131, 133, 134, 135, 154, 155, 172,
O T A '1177 1 4	176, 180, 184, 186, 187, 243, 249, 254, 256, 260, 289, 317, 318
C. I. Acid Violet	7, 11, 15, 34, 35, 41, 43, 49, 75
C. I. Acid Blue	1, 7, 9, 22, 23, 25, 27, 29, 40, 41, 43, 45, 49, 51, 53, 55, 56, 59,
	62, 78, 80, 81, 83, 90, 92, 93, 102, 104, 111, 113, 117, 120,
G I A -: 1 C	124, 126, 145, 167, 171, 175, 183, 229, 234, 236
C. I. Acid Green	3, 12, 19, 27, 41, 9, 16, 20, 25
C. I. Acid Braun	4, 14
As basic dyes:	2.9
C. I. Basic Black	2, 8
C. I. Basic Yellow	1, 2, 11, 12, 14, 21, 32, 36
C. I. Basic Orange	2, 15, 21, 22
C. I. Basic Red	1, 2, 9, 12, 13, 37
C. I. Basic Violet	1, 3, 7, 10, 14

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C. I. Basic Blue
                           1, 3, 5, 7, 9, 24, 25, 26, 28, 29
C. I. Basic Green
                           1, 4
C. I. Basic Braun
                           1, 12
As reactive dyes:
C. I. Reactive Black
                           1, 3, 5, 6, 8, 12, 14
C. I. Reactive Yellow
                           1, 2, 3, 13, 14, 15, 17
C. I. Reactive Orange
                           2, 5, 7, 16, 20, 24
C. I. Reactive Red
                           6, 7, 11, 12, 15, 17, 21, 23, 24, 35, 36, 42, 63, 66
C. I. Reactive Violet
                           2, 4, 5, 8, 9
C. I. Reactive Blue
                           2, 5, 7, 12, 13, 14, 15, 17, 18, 19, 20, 21, 25, 27, 28, 37, 38, 40,
                           41, 71
C. I. Reactive Green
                           5, 7
C. I. Reactive Braun
                           1, 7, 16
As pigments for food:
C. I. Food Black
                           2
C. I. Food Yellow
                           3, 4, 5
C. I. Food Red
                           2, 3, 7, 9, 14, 52, 87, 92, 94, 102, 104, 105, 106
C. I. Food Violet
C. I. Food Blue
                           1, 2
C. I. Food Green
                           2, 3
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As liquid medium of the ink, we can name water and any kind of water soluble organic solvent, for example, methyl alcohol, ethyl alcohol, n – propyl alcohol, isopropyl alcohol, n- butyl alcohol, sec - butyl alcohol, tert - butyl alcohol, isobutyl alcohol, and such kinds of alkyl alcohol of $1 \sim 4$ carbons; dimethyl formamide, dimethyl aceto amide and such kinds of amide; acetone, diacetone alcohol and such kinds of ketone or ketone alcohol; tetra hydro furan, dioxane and such kinds of ether; polyethylene glycol, polypropylene glycol and such kinds of polyalkylene glycol; ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, 1, 2, 6 – hexane triole, thio diglycol, hexylene glycol, diethylene glycol and such kinds of alkylene glycol of $2 \sim 6$ alkylene groups; glycerine, ethylene glycol methyl ether, diethylene glycol methyl (or ethyl) ether, triethylene glycol monomethyl ether and such kinds of lower alkyl ether of polyhydric alcohol, etc.

Among these numerous water soluble organic solvents, the preferable ones are diethylene glycol and such polyhydric alcohol, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether and such lower alkyl ether of polyhydric alcohol.

As other additives we can name, for example, PH conditioning agents, sequestering agents, anti - mold agents, viscosity conditioning agents, surface tension conditioning agents, wetting agents, surface active agents, and anti - rust agents etc.

Thanks to our invention the light resistance of the image improves when we do the recording using aqueous ink that contains water soluble dye on a recording medium that contains hindered amine type compound. The reason for this is not clear, but we may assume that fading and discoloring of the dye is caused by a radical, which is produced on top of the dye molecule due to ultraviolet rays, etc., and since the hindered amine type compound traps and stabilises this radical that was produced, we may assume that the decomposition of the dye is probably restrained.

The measuring of the ink jet adaptability happened according to the methods below.

For the light resistance, we irradiated the image parts that were obtained by doing solid printing with C, M, Y, Bk ink respectively, using an ink jet printer made by Canon (A – 1210), for 40 hours at 40 $^{\circ}$ C, 60 $^{\circ}$ K, illumination 60 w / 2 , with a Xenon Fade Meter (made by Suga Shikenki Co., FAL – 25 X – HCL model), measured the color density before and after irradiation with a MacBeth densitometer RD 514, and indicated the white part percentage, being a value for which we subtracted the color density after irradiation from the color density before irradiation (remaining percentage), as light resistance. For the discoloring and fading, we judged with the naked eye how much change in red of the black print image part there was at this moment.

For the water resistance we dipped the image parts that were obtained by doing solid printing with C, M, Y, Bk ink respectively, using the same ink jet printer made by Canon, for 3 minutes in running water of 30 °C, measured the density before and after the immersion with a MacBeth densitometer RD 514, and took the white part percentage, for which we subtracted the density after dipping from the density before dipping, as the value of the water resistance. The higher the value, the better the water resistance.

For the ink absorption speed we forwarded the paper right after (about 1 second after) solid printing of red letters (magenta + yellow), using an ink jet printer made by Sharp or Canon, touched it with a paper press roll or a finger, etc., and judged whether or not there was pollution.

(E) Examples of implementation

Below we will explain our invention by giving examples of implementation, but it is not limited to these examples. The 'parts' and '%' in the examples of implementation mean weight parts and weight %.

Example of implementation 1

In pulp slurry consisting of 70 parts of LBKP of freeness 350 ml csf and 30 parts of NBKP of freeness 400 ml csf, we added 18 parts of heavy calcium carbonate, 1 part of cation starch and 0.01 parts of anionic high molecular weight yield improvement agent, and made paper with a basis weight of 68 g/m² with a long rope paper making machine. With a size press installation, which was placed halfway the paper making machine, we attached a size press solution at 60 g/m² with water included, for which 3 parts of polyvinyl alcohol (PVA 117 made by Kurare [Clare?] Co.), 2 parts of cationic resin (Neofix RP – 70 made by Nikka Kagaku Co.) and 0.2 parts of the hindered amine compound that has the structure formula below were dissolved in 94.8 parts of water containing acetic acid, dried it, finished it according to the usual methods, and took this as paper for recording of Example 1. We measured the ink jet adaptability of this paper for recording, and the results are shown in Table 1.

Hindered amine compound See Japanese text p. 7 (2, 2, 6, 6 – tetramethyl – 4 – piperidyl – benzoate)

Comparative example 1

Except that we omitted the hindered amine compound from the size press solution that was used in Example 1, we did exactly the same as in Example 1, and thus obtained paper for recording of Comparison 1. We measured the ink jet adaptability of this paper for recording, and the results are shown in Table 1.

Example of implementation 2

From a slurry consisting of 80 parts of LBKP of freeness 370 ml csf, 20 parts of NBKP of

freeness 400 ml csf, 13 parts of heavy calcium carbonate, 1 part of cation starch, 0.08 parts of alkyl ketene dimer sizing agent (Hercon W, made by Dick Hercules Co.), and 0.4 parts of polyalkylene polyamine epichloro hydrine resin, we made raw paper with a basis weight of $68 \text{ g} / \text{m}^2$ with a long rope paper making machine. At the moment of the paper making we attached starch oxide with a size press installation at $2 \text{ g} / \text{m}^2$ in solid part, and thus made coat raw paper. The Steckigt sizing degree of this raw paper was 21 seconds.

As coating solution, we made a solution of 18 % solid part, consisting of 100 parts of synthetic silica (Mizuka Sil P - 73, made by Mizusawa Kagaku Co.), 20 parts of polyvinyl alcohol (PVA 117 made by Kurare Co.) and a small amount of defoaming agent, coated and dried this on the coat raw paper mentioned earlier with an air knife coater, so that the solid part became 11 g/m², and thus made base paper that has an ink reception layer.

Separately we coated and dried a solution, for which we dissolved 1 part of the hindered amine compound that has the structure formula below in 99 parts of water containing acetic acid, on the surface of the base paper mentioned earlier as coating solution, so that the solid part became $0.2 \text{ g} / \text{m}^2$, next lightly did supercalendering, finished it, and took this as paper for recording of Example 2.

We measured the ink jet adaptability of this paper for recording, and the results are shown in Table 1.

Hindered amine compound See Japanese text p. 8 {bis - (1, 2, 2, 6, 6 - pentamethyl - 4 - piperidyl) sebacate}

Comparative example 2

Except that we used a solution of solvent only, which did not contain the hindered amine compound of the coating solution that was used in Example 2, we did exactly the same as in Example 2, and thus obtained paper for recording of Comparison 2. We measured the ink jet adaptability of this paper for recording, and the results are shown in Table 1.

Examples of implementation $3 \sim 8$

As coating solution, we made 6 kinds of coating solution of 18 % solid part, consisting of 100 parts of synthetic silica (Fine Sil X - 37, made by Tokuyama Sotatsu Co.), 20 parts of polyvinyl alcohol (PVA 117 made by Kurare Co.), 7 parts of cationic resin (Polyfix 601, made by Showa Kobunshi Co.), 0.1, 0.5, 1, 2, 4, 8 parts respectively of the hindered amine compound that has the structure formula below, and a small amount of defoaming agent, coated and dried each of them on the same coat raw paper that was used in Example 2 with an air knife coater, so that the solid part became $14 \text{ g} / \text{m}^2$, lightly did supercalendering, and took these as papers for recording of Examples 3, 4, 5, 6, 7, 8, which have an ink reception layer that contains hindered amine compound. We measured the ink jet adaptability of these papers for recording, and the results are shown in Table 1.

Hindered amine compound See Japanese text p. 8 {bis - (2, 2, 6, 6 - tetramethyl - 4 - piperidyl) phtalate}

Comparative example 3

Except that we omitted the hindered amine compound from the coating solution that was used in Example 3, we did exactly the same as in Example 3, and thus obtained paper for recording of Comparison 3. We measured the ink jet adaptability of this paper for recording, and the results are shown in Table 1.



EUROPEAN SEARCH REPORT

Application Number

EP 02 10 2340

	Citation of document with		, , , , , , , , , , , , , , , , , , , 	01.400/5/5/5
Category	Citation of document with of relevant par	indication, where appropriate, ssages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CI.7)
Α	"Ink jet recordin hindered amine cpd 4-benzoyloxy-2,2,6 piperidine or 2,2,6,6-tetra:meth DERWENT, XP002225590 * abstract *	,6-tetra:methyl	1	B41M5/00 C07D211/72 C07D211/62 C07D211/94 C07D211/58 C07D207/16 C07D405/12 C07D405/14
Α	WO 01 20078 A (CIB. 22 March 2001 (200 * page 4, line 11 * examples *	1-03-22)	8	
				TECHNICAL FIELDS SEARCHED (Int.CI.7
				C07D
	The present search report has	been drawn up for all claims		
	Place of search THE HAGUE	Date of completion of the search 3 March 2003	Mark	Examiner Cham, R
. CA X : partic Y : partic docur A : techn	TEGORY OF CITED DOCUMENTS cularly relevant if taken alone cularly relevant if combined with anot nent of the same category ological background written disclosure	T : theory or princi E : earlier patent d after the filing d her D : document cited L : document cited	ple underlying the in ocument, but publis ate in the application	evention hed on, or

Table 1

item	Ink absorption	Fading and	Light	resista	nce (%	5)	Water	e (%)		
paper for	speed	discoloring	M	С	Y	Bk	M	С	Y	Bk
recording										
Example 1	O O 74 100 100 100		100	111	104	111	105			
Comparison 1	0	X	29	99	76	74	110	105		
Example 2	0	Ο	93	100	97	94	16	68	11	19
Comparison 2	0	X	62	93	96	76	11	49	8	18
Example 3	0	(Δ)	83	100	94	92	96	100	97	96
" 4	0	O	84	100	95	94	97	100	96	97
" 5	0	0	84	100	94	94	96	101	95	95
" 6	0	О	84	100	96	95	96	100	94	96
" 7	0	О	85	100	96	95	94	100	95	95
" 8	8 O O 85 100 97 95 95 102		102	93	95					
Comparison 3	0	X	71	87	85	78	95	100	83	96

(F) Efficiency of the invention

As is clear from Table 1, we could see that, compared to the comparative examples, the examples of implementation $1 \sim 8$, which contain the hindered amine compound inside the recording medium in accordance with our invention, showed improved results, with the fading and discoloring of the black ink image and the light resistance of the black ink image and magenta ink image being very excellent.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 92 10 2340

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European sarch report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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